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Seventh Technical Report

OXYGEN ATOM TRANSFER PROCESSES

October 1953

Henry Taube

University of Chicago

Department of Chemistry

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Mechanism of Aquotization of Carbonato Complex Ions

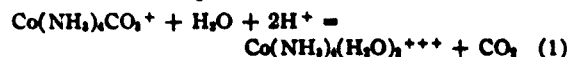
By Franz A. Posey and Henry Taube

Mechanism of Aquotization of Carbonato Complex Ions

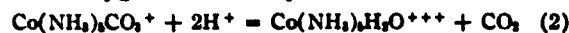
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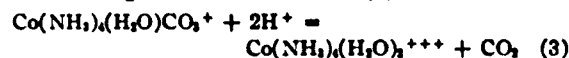
Stranks and Harris¹ have reported that there is no carbon isotope discrimination in the reaction



In an oxygen tracer study on a related reaction



Hunt, Rutenberg and Taube² showed that in release of carbonate, the Co-O bond is not severed, but rather the C-O bond. Since reaction (2) is analogous to what can reasonably be supposed to be a stage in the net reaction (1)



there is an apparent inconsistency in the two observations which, while it can be resolved by one of several assumptions, forces none as a conclusion. We have therefore undertaken an oxygen tracer study of reaction (1), for comparison with the results obtained in reaction (2), similar to that conducted for this reaction, but have increased the power of the tracer results by examining also the isotopic composition of the carbon dioxide liberated both in reactions (1) and (2). The method for isotopic assay of the water bound in $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{+++}$ was developed during the course of other research on the ion, and will be described more fully when these results are published.

Experimental

The salt $(\text{Co}(\text{NH}_3)_4\text{CO}_3)\text{NO}_3 \cdot 1/2\text{H}_2\text{O}$ was prepared according to the method of Grubitsch.³ The purity was checked by electrolytic determination of the cobalt content (calculated, 22.84%; observed, 22.86%). The salt $(\text{Co}(\text{NH}_3)_4\text{CO}_3)\text{NO}_3 \cdot \text{H}_2\text{O}$ was part of a preparation used previously.³

The tracer experiments with $(\text{Co}(\text{NH}_3)_4\text{CO}_3)\text{NO}_3 \cdot 1/2\text{H}_2\text{O}$ were performed by preparing a solution of this compound in water enriched in H_2O^{18} . Perchloric acid in water of isotopic composition very near to that in the solution was then added. During this operation, a rapid stream of nitrogen passed through the solution to carry off the carbon dioxide released. This was stripped from the gas by means of a trap immersed in liquid nitrogen. The ion $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{+++}$ was precipitated from the solution with $\text{Co}(\text{CN})_6^{4-}$, and the salt $(\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2)(\text{Co}(\text{CN})_6)$ was removed, washed, dried, and finally heated *in vacuo* to remove the complex-bound water. The isotopic composition of the water was determined by equilibrating it with carbon dioxide, and analyzing the carbon dioxide in a mass spectrometer. The necessary blank determinations were conducted as indicated by the procedures described. Separate experiments were also conducted in which the solid carbonate salts were dusted into perchloric acid in enriched water, and the carbon dioxide swept out with nitrogen as before.

All operations were performed as rapidly as possible to minimize exchange of $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$ and $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{+++}$ with the environment. The solutions before addition of the acid were cooled to 0°, and maintained there for precipitation of $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2(\text{Co}(\text{CN})_6)$. In a typical experiment, 1.5 g. of salt was used in 30 ml. of solution.

Results

N represents the mole fraction of O^{18} in the species under

(1) D. R. Stranks and G. W. Harris, *J. Phys. Chem.*, **56**, 906 (1952).

(2) J. P. Hunt, A. C. Rutenberg and H. Taube, *THIS JOURNAL*, **74**, 298 (1952).

(3) H. Grubitsch, "Anorganisch-präparative Chemie," Springer Verlag, Vienna, 1950, p. 441.

consideration. All results were normalized to 2.000×10^{-3} as the mole fraction of O^{18} in a sample of ordinary CO_2 kept as a standard.

The method of isotopic assay of $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{+++}$ was tested by precipitating the cobalticyanide from water enriched in O^{18} , after leaving the aquo ion in contact under conditions and for a time comparable to those obtaining in the experiments with the carbonate ion. The results were: $N \times 10^3$ for inner sphere water of $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{+++}$ precipitated from normal water = 2.235; $N \times 10^3$ for normal water = 1.928; $N \times 10^3$ for inner sphere water when precipitated from enriched solvent = 2.348; $N \times 10^3$ for H_2O in enriched solvent = 7.163. The results show 2.3% exchange of the aquo ion during the operation.

To learn the exchange to be expected for CO_2 liberated by acid under the conditions of our experiments, a solution of Na_2CO_3 (of normal isotopic composition) was added to enriched water containing acid, with the following results: $N \times 10^3$ for CO_2 from Na_2CO_3 in ordinary water = 1.906; $N \times 10^3$ for CO_2 from Na_2CO_3 in enriched water = 2.077; $N \times 10^3$ for enriched water = 5.985; exchange of CO_2 = 2.0%.

To provide the necessary base values for the interpretation of the tracer experiments, the aquotization of $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$ was conducted in water of normal isotopic composition ($N \times 10^3 = 1.928$). $N \times 10^3$ for CO_2 from aquotization = 2.009; $N \times 10^3$ for inner sphere water = 1.985.

The results on the aquotization in enriched water are: $N \times 10^3$ for water in solution = 8.263; $N \times 10^3$ for inner sphere water = 5.147. Base value (1.985×10^{-3} corrected for exchange expected in this environment = 2.129×10^{-3}). Fraction of inner sphere water derived from environment = 0.493. The carbon dioxide collected in this experiment was found to have undergone 5.4% exchange with the environment, somewhat in excess of that observed using Na_2CO_3 . A third experiment proved this exchange not to be reproducible (~8%), and the method of adding the solid was adopted.

With $(\text{Co}(\text{NH}_3)_4\text{CO}_3)\text{NO}_3 \cdot 1/2\text{H}_2\text{O}$, the results were: $N \times 10^3$ for H_2O in enriched solvent = 6.923; $N \times 10^3$ for CO_2 released = 2.069. The value 2.069 compared with 2.009 for the release of CO_2 in normal water shows 1.2% enrichment.

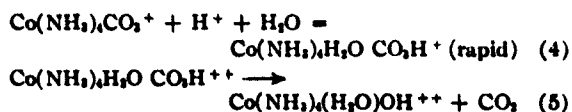
With $(\text{Co}(\text{NH}_3)_4\text{CO}_3)\text{NO}_3 \cdot \text{H}_2\text{O}$ the results were: $N \times 10^3$ for CO_2 released from normal water = 1.972; $N \times 10^3$ for CO_2 released from enriched water = 2.048; $N \times 10^3$ for H_2O in enriched solution = 5.665. In this experiment, the carbon dioxide underwent 1.5% exchange with the solvent.

Discussion

It is necessary for the success of an experiment of this type that the resulting aquo ion not exchange rapidly with the solvent. The blank experiments with $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{+++}$, as well as proving the method of isotopic analysis of the bound water, prove the formula of this ion in water to be $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{+++}$, and demonstrate its exchange with the solvent to be sufficiently slow for the present purposes.

The experiments show that the ion $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{+++}$, formed from $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$, derives only 1/2 of the oxygen from the solvent, the other 1/2 being left by the carbonate when CO_2 is removed. The possibility that the 50% exchange appears equally distributed between the two positions, as an accidental value on the way to complete exchange, can be excluded by considering the isotopic composition of the liberated CO_2 . Such enrichment could only take place with some form of the carbonate ion ($\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{+++}$ does not exchange sufficiently rapidly) and would necessarily result in enrichment of the CO_2 which is liberated. The slight enrichment of the CO_2 , observed (~1%) is attributable to exchange following its release.

Stranks and Harris have suggested the mechanism



The stepwise feature of the mechanism is certainly reasonable, and is to some extent confirmed by providing an explanation for our oxygen tracer results. Applying our observations to this mechanism, it can be concluded that the Co-O bond is severed in step (4), otherwise CO_2 would appear at least 33% exchanged with solvent. Reaction 5, involving $\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}^* \text{CO}_3\text{H}^{++}$, then takes place as demonstrated for the analogous ion $\text{Co}(\text{NH}_3)_4\text{CO}_3\text{H}^{++}$, severing the C-O bond. The fractionation experiments of Stranks and Harris, obtained for the reaction in acid, find an explanation if reaction (4) under these conditions is formulated not as an equilibrium, but as a rate determining step; no large carbon fractionation can be expected in step (4) since the Co-O bond is severed there, and none can take place in (5), since the ion is completely decomposed to products.

It is interesting to note that the major conclusions are indicated also by the experiments on aquotization in ordinary water, the isotopic composition of the inner sphere water (1.985×10^{-3}) lying fairly near the mean of that of the solvent (1.928×10^{-3}) and of the carbon dioxide (2.009×10^{-3}). The dependability of such a conclusion drawn from this experiment, however, is reduced not only because of the slight difference between the extreme values, but also because fractionation effects interfere. These can take place due to discrimination by Co(III) between O^{16} and O^{18} in water, and in the attached carbonate. The results show that a slight excess of O^{18} is left on the Co(III).

If it is assumed that precisely 50% of the H_2O in the inner sphere is derived from the solvent, the isotopic composition expected for this water in the

experiment using enriched solvent is the mean of 8.263×10^{-3} and 2.009×10^{-3} or 5.136×10^{-3} . When this is corrected for the exchange to be expected for the aquo ion, the value 5.208×10^{-3} is obtained, to be compared with the experimental value of 5.147×10^{-3} . The result may indicate a slightly greater rate of reaction of H_2O^{18} compared to H_2O^{16} .

A conclusion about mechanism which applies to the results for CO_3^- attached as a chelate, bound at one position, or not bound at all, is that there is no transfer of oxygen from the solvent to C at any stage on the release of CO_2 . Thus it seems likely that the activated complex which in the case of $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$ has the composition $\text{Co}(\text{NH}_3)_4\text{CO}_3\text{H}^{++}$, does not have the structure reasonable for this complex ion, but rather has the proton on the oxygen bridging cobalt and carbon



Since new Co(III) bonds are established during the release of CO_2 from $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$, it will be of interest to learn whether groups besides water (e.g., Cl^- , SO_4^-) can enter during this rapid process. It was this possibility that attracted interest to the aquation of $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$, but could not be realized in this reaction since oxygen is left attached to Co(III).

Acknowledgments.—This work was supported by the Office of Naval Research under contract N6-ori-02026. The funds for the purchase of the mass spectrometer used in the research were supplied by the Atomic Energy Commission under contract At(11-1)-92.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO
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Observations on the Mechanism of Electron Transfer in Solution

By Henry Taube, Howard Myers, and Ronald L. Rich

OBSERVATIONS ON THE MECHANISM OF ELECTRON TRANSFER IN SOLUTION¹

Sir:

An important problem in the field of mechanisms of "electron transfer" reactions is concerned with the changes taking place in the coordination spheres of the oxidant and the reductant on electron transfer. This problem has been but little elucidated for reaction of cations, as for example $Ti^{+++} + Fe^{+++} = Ti(IV) + Fe^{++}$ (net change) or $Fe^{*++} + Fe^{+++} = Fe^{*+++} + Fe^{++}$ (virtual change). Thus it is not known whether electron transfer takes place by an electron jump through several layers of solvent, or whether it accompanies the transfer of a group such as OH from oxidant to reductant; or H from reductant to oxidant.² Similarly the particular role played by negative ions such as Cl^- or F^- in catalyzing^{3,4,5} the reaction of cations is not understood. The principal reason for the lack of a detailed understanding is that the systems are generally very labile with respect to changes in the coordination sphere so that intermediate stages which would supply evidence about the nature of the activated complexes change to final products too rapidly for convenient observation. One method of attack on these problems is to alter conditions so as to slow up the changes; another is to exploit the ions which are less labile with respect to substitution under ordinary conditions.

We have followed the latter line of attack, choosing the reductant $Cr^{++} \rightarrow Cr(III)$. This system has the virtue that any group found in the coordination sphere of $Cr(III)$ when it is formed from Cr^{++} must have been present in the activated complex. Substitution reactions on $Cr(III)$ are sufficiently slow so that entry of groups after completion of the oxidation can be ruled out at least for some systems. (For $Cr(II)$, however, substitutions are rapid⁶.)

A significant result is that when Cr^{++} is oxidized by Fe^{+++} in perchloric acid medium (1 M) in a solution containing Cl^- (0.05 M), chloride ion is found attached to the product $Cr(III)$ (0.5 mole/mole $Cr(III)$ for these conditions). Hence, we can conclude that $Cl-Cr$ bonds must have been established in the activated complex. The experiments, however, do not distinguish the activated complexes $[Cr-Cl-Fe]^{+4}$ (implying Cl

atom transfer as the act producing electron transfer) or $[ClCr^{+} \cdot water \cdot Fe^{+++}]$ (implying electron transfer through the solvent facilitated by Cl^- attached to Cr^{++}). A decision in favor of the former type of explanation is reached on the basis of experiments we have done using as oxidizing agents complex ions which are slow with respect to substitution. We find that when $Co(NH_3)_6Cl^{++}$ is reduced by Cr^{++} in 1 M $HClO_4$, one Cl^- appears attached to chromium for each $Cr(III)$ which is formed or $Co(III)$ reduced. Furthermore, when the reaction is carried out in a medium containing radioactive chloride, the mixing of the Cl^- attached to $Cr(III)$ with that in solution is found to be less than 0.5%. The experiment with radioactive chloride shows that transfer of chlorine from the oxidizing agent to the reducing agent is direct, rather than by release and reentry of Cl^- , and leads to the formulation of the activated complex as $[(NH_3)_6Co-Cl-Cr]^{+4}$ (apart from the participation

by solvent and its ions). Transfer from $Co(NH_3)_6Br^{++}$ to $Cr(III)$ is also found to be complete. In both cases the net changes are to form $Cr(H_2O)_6^{+++}$ and X^- as final products, with, however, CrX^{++} as a recognizable intermediate stage.

The observations on relative rates are also significant. Rates of reduction increase in the order: $Co(NH_3)_6^{+++}$, $Co(NH_3)_5H_2O^{+++}$, $Co(NH_3)_5Cl^{++}$, $Co(NH_3)_5Br^{++}$. The groups H_2O , Cl^- and Br^- have available pairs of unshared electrons as points of attack, the polarizability of the groups increasing in the order named. With $Co(NH_3)_6^{+++}$, a proton must be removed to provide a pair of electrons as point of attack for Cr^{++} , or the electron must be transferred through the proton coordination shell.

We propose an activated complex of the type $[(NH_3)_6Co-X-Cr]^{+4}$ as a model for processes in which negative ions catalyze electron exchange between cations. Experiments are in progress to determine whether oxygen atom transfer occurs in the reaction of Cr^{++} with $Co(NH_3)_5H_2O^{+++}$. These have significance in their relation to processes involving activated complexes such as $[Ti^{+++} \cdot Fe^{+++}]_{aq.}$, $[Fe^{++} \cdot Fe^{+++}]_{aq.}$, etc. We recognize that an activated complex of the type we have formulated is not always readily accessible, as for example, when both partners are inert to substitution changes. When at least one partner is labile, the direct bridge complex seems a likely path.

(1) This work was supported by the Office of Naval Research under Contract N6-Ori-03026.

(2) See W. F. Libby, "Symposium on Electron Transfer and Isotopic Reactions," *J. Phys. Chem.*, **56**, 853 (1952); discussion by R. W. Dodson, N. Davidson, O. L. Forchheimer, pp. 866, et seq.

(3) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

(4) D. J. Meier and C. S. Garner, *ibid.*, **56**, 853 (1952).

(5) H. C. Hornig and W. F. Libby, *ibid.*, **56**, 866 (1952).

(6) H. Taube, *Chem. Reviews*, **50**, 99-101 (1952).

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RECEIVED JULY 6, 1953

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**The Study of a System Involving Equilibrium
between Inner Sphere and Outer Sphere
Complex Ions: $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{+++}$ and SO_4^-**

By Henry Taube and Franz A. Posey

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES, UNIVERSITY OF CHICAGO]

The Study of a System Involving Equilibrium between Inner Sphere and Outer Sphere Complex Ions: $\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}^{+++}$ and SO_4^-

BY HENRY TAUBE AND FRANZ A. POSEY

RECEIVED OCTOBER 10, 1952

The fractional conversion of $\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}^{+++}$ to $\text{Co}(\text{NH}_3)_4\text{SO}_4^+$ at equilibrium is observed to be almost independent of the concentration of sulfate ion over a wide range above ca. 0.01 *M*. The behavior is understood if the aquo ion is assumed to be converted to a sulfate complex ion by outer sphere association at low concentration of sulfate ion. The interpretation is confirmed by observations on the ultraviolet absorption band of $\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}^{+++}$ in the presence of varying amounts of sulfate ion. The change from the sulfato ion to the "isomeric" outer sphere complex ion is governed by the energy quantities: $\Delta H = -4.0 \pm 0.3$ kcal. mole⁻¹, $\Delta S = -13$ cal. deg.⁻¹ mole⁻¹. The reactions are first order in the concentration of $\text{Co}(\text{III})$. An increase in lability is observed with increase in sulfate ion concentration. The reactions are catalyzed by hydrogen ion. The activation energy for the change of the sulfato ion to the aquo ion is 19.3 ± 0.5 and for the reverse change is 23.7 ± 0.5 kcal. mole⁻¹.

In considering the structure in solution of a complex ion the stoichiometry of which has been established, the question arises as to its distribution between two forms, in one of which the addend is directly attached to the central ion occupying a position in the first sphere of coordination, and in the other occupying a position outside the first sphere of coordination. The latter type of structure can be expected to have considerable stability when the central ion has a high charge and when the addend is an ion of high charge. The importance of association of this type in water solution has been proven by the work of Davies,¹ Linhard² and Katzenellenbogen³ using complex cations of the type $\text{Co}(\text{NH}_3)_4^{+++}$. Replacement of NH_3 by the anion does not take place under the conditions which were chosen and, in fact, the observations on the spectra³ suggest that the first sphere of coordination is little disturbed in forming the outer sphere complex ions. It is evident that inert complex ions are extremely useful in defining the type of association under study, owing to the great difference in the speed at which association in the inner sphere and outer spheres takes place. For labile complex ions the distinction between the two types is much more difficult to make because the two forms are not readily separately characterized.

We have made use of an inert complex ion system also in our study. Substitution of water by water or other groups in $\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}^{+++}$ takes place very slowly.⁴ Our data with this cation and with SO_4^- as an anion provide a dramatic demonstration of the presence in the solution of outer sphere complex ions, and furthermore, since H_2O and SO_4^- are eventually exchanged, have made possible a comparison of the stabilities of inner sphere and outer sphere "isomeric" forms. The desirability of a more complete study of this system was indicated by work done on the water exchange reaction.⁴ The experiments we are reporting supplement those described by Adell.⁵ His study was limited to the range of dilute solutions ($(\text{SO}_4^-) \sim 10^{-3}$ or less) and therefore did not expose some of the interesting phenomena we have observed.

Experimental

The procedure was to follow the extinction of a solution containing initially the ion $\text{Co}(\text{NH}_3)_4\text{SO}_4^+$ or $\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}^{+++}$ in an environment of known composition as a function of time. In all cases equilibrium was approached from both sides, and in every case the final values of the extinction agreed to within 1%. For numerous solutions the rate was followed as a function of time starting for a given environment both with the sulfato and the aquo ion. In every case tested the specific rates *k* (defined as below), forward and reverse, agreed to within 3% if only total sulfate were present in sufficient excess. The values of the initial optical densities for the sulfato and aquo forms, and of the final optical density make possible the calculation of the equilibrium quotient, and these data, together with the specific rate for approach to equilibrium, lead to the specific rate of aquotization and sulfato formation for each solution. The optical densities were measured using a Beckman spectrophotometer. The wave length 560 μ at which the extinctions were measured lies on the long wave length side of a band with a maximum at 515 μ for the sulfato and 495 for the aquo ion. The two maxima in the visible for the ions are not sufficiently well separated to make them useful in analyzing the solution. While the strong ultraviolet band does differ markedly for the two substances, light of longer wave length was preferred since it permitted the use of Corex cells. The extinctions of $\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}^{+++}$ and $\text{Co}(\text{NH}_3)_4\text{SO}_4^+$ at λ 560 μ are changed somewhat (cf. Table I) as the environment changes, but only slightly as compared to the ultraviolet band. It was shown that the cobalt cations obey Beer's law in the solutions studied within experimental error. The extinctions change slightly with temperature—for example, there is an increase of ca. 3% in the extinction of the sulfato ion in 0.05 *M* Na_2SO_4 as temperature rises from 25 to 31°—hence for a series all extinction measurements were made at constant ($\pm 1^\circ$) temperature. In studying the variation of equilibrium constant with temperature the solutions which had been stored at different temperatures were all brought to the same temperature for comparison of optical densities. No significant readjustment in the inner sphere of coordination took place during the temperature change.

The substance $[\text{Co}(\text{NH}_3)_4\text{SO}_4]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$ was the source of the sulfato ion. It was prepared as described by Jorgensen.⁶ The content of Co and SO_4 were found to be 15.80% (theoretical, 15.79) and 51.42% (theoretical, 51.47). $\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}(\text{ClO}_4)_2$ was prepared as described elsewhere,⁴ and served as the source of the aquo ion. The agreement of final optical densities starting with both salts shows that the aquo salt was a sufficiently good preparation. Other reagents were of A. R. quality, used without further purification. Solutions were made up using redistilled water.

Conditions and Definitions.—In all experiments except expt. 11, Table I, the concentration of sulfate was in excess of the concentration of the complex ion by a factor of 8 or greater. Over the greater part of the range investigated, the specific rate as well as the equilibrium distribution is not very sensitive to the concentration of SO_4^- , and the initial recorded values which differ at most by 7 or 8% from the equilibrium values, serve as sufficiently good de-

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TABLE I
DATA ON EQUILIBRIUM DISTRIBUTION AND RATE AS FUNCTION OF SULFATE CONCENTRATION
Temperature $31.1 \pm 0.02^\circ$, except in expt. 8; SO_4^{2-} as Na_2SO_4 except in expts. 5 and 6

No.	$\Sigma[\text{SO}_4^{2-}]$	$\Sigma[\text{H}^+]$	$k \times 10^4$	D^S	D	D^A	Q_e	$k_A \times 10^4$	$k_S \times 10^4$
1	2.90	0.30	11.3	0.491	0.328	0.213	1.42	6.6	4.7
2	1.15	.11	8.3	.495	.339	.214	1.25	4.6	3.7
3	0.57	.050	6.8	.501	.345	.213	1.18	3.7	3.1
4	.156	.015	4.8	.499	.345	.214	1.17	2.6	2.2
5	.156 ^a	.015	4.3	.499	.347	.214	1.14	2.3	2.0
6	.156 ^b	.015	5.2	.502	.348	.215	1.16	2.8	2.4
7	.052	.010	4.1	.506	.352	.214	1.12	2.2	1.9
8 ^c	.052	.010	17.0	.506	.371	.214	0.86	7.9	9.1
9	.021	.010	3.4	.508	.345	.217	1.28	1.9	1.5
10	.0140	.010	2.8	.510	.341	.217	1.36	1.7	1.2
11 ^d	.00216	.0061		.512	.321	.221	1.91		

^a K_2SO_4 . ^b MgSO_4 . ^c Temperature 43.8° . ^d $(\text{RSO}_3\text{HSO}_3) = 0.00108 M$; $(\text{HClO}_4) = 0.005 M$. No other electrolyte.

descriptions of the sulfate concentration prevailing. Except where otherwise recorded, sulfate was introduced as Na_2SO_4 .

$\Sigma[\text{SO}_4^{2-}]$ refers to total SO_4^{2-} present, whether complexed or not (and differs but slightly from uncomplexed sulfate as noted above)

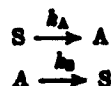
$\Sigma[\text{H}^+]$ represents concentration of H^+ present in all forms R represents the radical $\text{Co}(\text{NH}_3)_6$

[A] represents the total concentration of species containing $\text{RH}_2\text{O}^{+++}$

[S] represents the total concentration of species containing RSO_3^+

D^S , D^A and D_e represent the optical densities ($\log I_0/I$) of solutions containing S initially, A initially and the equilibrium mixture, respectively. For all solutions, $cd = 0.0150 \text{ cm. mole l.}^{-1}$.

k is the specific rate of change as measured in a plot of $\log |D_0 - D_e|$ versus t . It is equal to the sum $k_A + k_S$ where these specific rates refer to the processes



Q_e represents the ratio $[A]/[S]$ at equilibrium and is equal to k_A/k_S .

Specific rates are expressed with time in minutes.

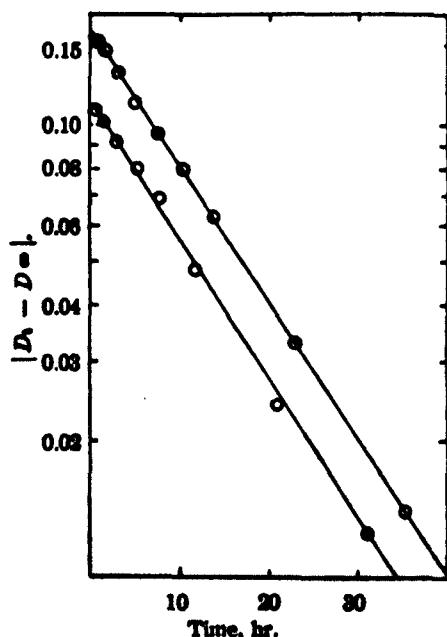


Fig. 1.—The variation of optical density with time medium, $\Sigma[\text{SO}_4^{2-}] = 2.90 M$, $\Sigma[\text{H}^+] = 0.3 M$. Upper curve, sulfate salt approaching equilibrium; lower curve, roseo salt. D same for both.

Results

In Fig. 1 are presented typical data on the change of optical density with time, starting in one experiment with the aquo salt and in another with the sulfate salt.

Table I contains a summary of results obtained at relatively low acidity with $[\text{SO}_4^{2-}]$ as the principal concentration variable. Acid was present in all solutions to suppress the acid dissociation of $\text{RH}_2\text{O}^{+++}$. The results reported later show that (H^+) (or (HSO_4^-)) is not an important variable at the levels used in the series in Table I.

Table II is a summary of the data obtained on the variation of Q_e with temperature. The data are shown plotted

TABLE II

VARIATION OF EQUILIBRIUM CONSTANT WITH TEMPERATURE

$\Sigma[\text{SO}_4^{2-}]$	Medium	$\Sigma[\text{H}^+]$	24.9°	Q_e at 31.1°	43.8°
2.90		0.30	1.67	1.42	1.11
0.052		.010	1.28	1.12	0.86
0.021		.010	1.44	1.27	1.01

in Fig. 2 to yield values of ΔH in kcal./mole which are as follows for the change: $S \rightarrow A$.

- -4.1 ± 0.3 at $2.6 M \text{ SO}_4^{2-}$
- -4.0 ± 0.3 at $0.052 M \text{ SO}_4^{2-}$
- -3.6 ± 0.3 at $0.021 M \text{ SO}_4^{2-}$

Table III presents data obtained for solutions containing also sodium perchlorate, Table IV for solutions with varying amounts of NaHSO_4 and Table V for solutions with varying amounts of NaHSO_4 and H_2SO_4 . In Table VI some data dealing with the changes in extinction for the ultraviolet band of $\text{RH}_2\text{O}^{+++}$ as SO_4^{2-} is added, are presented. The study of the spectra in solutions of various compositions is itself a major undertaking and more complete data for this and related systems will be presented in a future publication.

Discussion

The most interesting feature of the equilibrium data is that the ratio Q_e is almost independent of (SO_4^{2-}) over a wide concentration range, extending from 0.02 to $2.6 M$. It is further remarkable that this ratio instead of diminishing at high (SO_4^{2-}) , in fact shows a slight increase in this concentration region. These observations suggest that the principal equilibrium operating over the range studied is



If ion pair formation is essentially complete even at $0.02 M \text{ SO}_4^{2-}$ the change S to A involves species of the same stoichiometry with respect to Co(III) and SO_4^{2-} and hence also of the same charge. Therefore the effects of salts, including SO_4^{2-} , is expected to be relatively slight. In the region of

TABLE III
THE INFLUENCE OF NEUTRAL ELECTROLYTE
Temperature 31.1°

No.	$\Sigma[\text{SO}_4^{--}]$	$\Sigma[\text{H}^+]$	(NaClO ₄)	$k \times 10^4$	D_p^a	D_p^a	Q_e	$k_A \times 10^4$	$k_B \times 10^4$
1	0.021	0.010	0.93	1.92	0.516	0.225	4.40	1.57	0.355
2 ^a	.054	.010	.71	2.56	.511	.223	2.13	1.74	0.62
3	.156	.010	.54	4.38	.506	.218	1.28	2.46	1.92
4	.054	.010	2.00	2.04	.524	.226	2.68	1.49	0.554
5	.156	.010	1.70	2.68	.507	.218	1.90	1.56	1.12

^a The series was planned at constant μ , but insufficient NaClO₄ was inadvertently added in this experiment.

TABLE IV
THE INFLUENCE OF BISULFATE ION
Temperature 31.1°

No.	(Na ₂ SO ₄)	(NaHSO ₄)	(NaClO ₄)	$k \times 10^4$	D_p^a	D_p^a	Q_e	$k_A \times 10^4$	$k_B \times 10^4$
1	0.054	0.10	0.60	3.61	0.506	0.215	1.47	2.1	1.5
2	.054	.30	.40	4.62	.500	.215	1.85	2.6	2.0
3	.054	.70	.00	6.34	.499	.214	1.44	3.7	2.6
4	.54	.10	1.40	5.25	.503	.224	1.07	2.7	2.5
5	.54	.40	1.10	5.85	.500	.219	1.13	3.3	2.6
6	.54	1.50	0.00	9.02	.500	.214	1.42	5.4	3.6

TABLE V
RATE AND EQUILIBRIUM DATA FOR SOLUTIONS CONTAINING
NaHSO₄ AND H₂SO₄
Temperature 31.1°

No.	(NaHSO ₄)	(H ₂ SO ₄)	$k \times 10^4$	D_p^a	Q_e	$k_A \times 10^4$	$k_B \times 10^4$
1	0.00	3.00	16.1	0.488	2.87	11.9	4.2
2	1.00	2.00	12.5	.496	2.14	8.5	4.0
3	3.00	0.00	10.2	.496	1.61	6.3	3.9
4	0.00	6.00	27.5	.485	2.26	19.1	8.4
5	3.00	3.00	21.0	.488	1.94	13.9	7.1
6	5.00	1.00	18.5	.490	1.69	11.6	6.9
7	0.00	9.00	36.0	.480	1.40	21.	15.

TABLE VI
THE ULTRAVIOLET EXTINCTION COEFFICIENTS OF $\text{Co}(\text{NH}_3)_6\text{H}_2\text{O}^{+++}$ AT VARIOUS CONCENTRATIONS OF SULFATE ION

Temperature $27 \pm 1^\circ$; $\epsilon = 1/\text{cm} \log I_0/I$ in l. mole⁻¹ cm.⁻¹;
($\text{RH}_2\text{O}(\text{ClO}_4)_6$) = $8.0 \times 10^{-4} M$; (HClO_4) = 0.01 M

λ in m μ	0.000	0.0063	0.0125	0.0418	0.1040
270	15	26	34	42	44
280	31	76	89	112	118
290	143	257	288	338	360
295	336	503	538	618	650
240	762	990	1010	1120	1180
235	1620	1910	1940		

low sulfate ion concentration the equilibrium



presumably becomes important and $\text{RH}_2\text{O}^{+++}$ as well as $\text{RH}_2\text{O}^{+++}\text{SO}_4^{--}$ contributes to [A]. At high concentration of SO_4^{--} , Q_e will be altered by salt effects on equilibrium (I) or by further association of sulfate with the complex ions. However, the affinities of $\text{RH}_2\text{O}^{+++}\text{SO}_4^{--}$ and RSO_4^+ for sulfate ion appear to be about the same, since Q_e changes only slightly even at high sulfate concentration.

The conclusion that $\text{RH}_2\text{O}^{+++}$ and SO_4^{--} are strongly associated is supported by Davies' calculations¹ for the similar system $\text{Co}(\text{NH}_3)_6^{+++}$ and SO_4^{--} which yielded 3.3×10^3 as the equilibrium constant for the association reaction at

zero ionic strength and 25° . The conclusion is directly proven by the data in Table VI on the ultraviolet extinctions of $\text{RH}_2\text{O}^{+++}$ in the presence of varying concentrations of SO_4^{--} . Marked changes in the extinction are observed in the ultraviolet band, with the extinctions at 240 and 235 m μ approaching saturation values when (SO_4^{--}) is only $6 \times 10^{-3} M$. More complete data will be required to obtain values of equilibrium con-

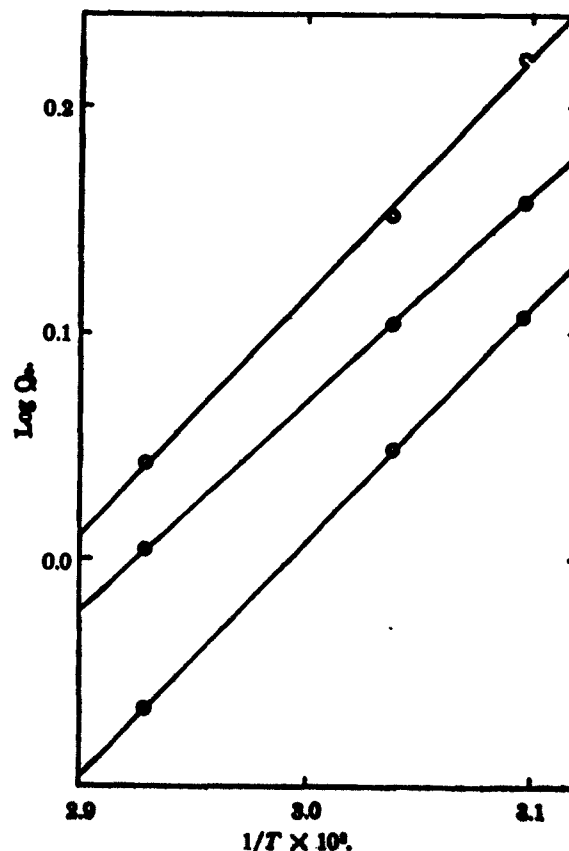


Fig. 2.—The variation of Q_e with temperature. Curves are in order for 2.90, 0.081 and 0.058 M, $\Sigma[\text{SO}_4^{--}]$ reading from top to bottom.

stants, particularly because successive stages of association apparently must be taken into account. This is evidenced by the observation that the rate of approach to saturation extinction values is different at different wave lengths.

If the assumption is made that the ratio $(\text{RH}_2\text{O}^{+++}\cdot\text{SO}_4^{--})/(\text{RSO}_4^+)$ remains constant below 0.05 *M* SO_4^{--} , and is measured by the ratio Q_e at this sulfate ion concentration, the value of K_{11} for expt. 11 is calculated as 1.1×10^3 . When corrected for the difference in μ , this value will be close to that reported by Davies for $\text{Co}(\text{NH}_3)_6^{+++}$ and SO_4^{--} .

The measured heats of reaction on the interpretation suggested apply to reaction I. It should be noted that the change is exothermic. It is interesting that the heat of transfer of SO_4^{--} from inner sphere to outer sphere does not change appreciably as (SO_4^{--}) changes from 0.05 to 2.6 *M*. The decrease in $|\Delta H|$ at lower (SO_4^{--}) can be attributed to participation by equilibrium (II). Using the observed values of equilibrium constant and ΔH at 0.05 *M* SO_4^{--} , ΔS at this concentration of sulfate is calculated as -13 e.u. An entropy decrease can be expected since ions of opposite charge are separated in transferring SO_4^{--} from inner sphere to outer sphere, thus increasing the interaction with the solvent.

The effect of NaClO_4 on the equilibrium $[\text{A}]/[\text{S}]$ is presumably largely in increasing the concentration of $\text{RH}_2\text{O}^{+++}$ relative to $\text{RH}_2\text{O}^{+++}\cdot\text{SO}_4^{--} + \text{RSO}_4^+$. There may also be an effect on the ratio $(\text{RH}_2\text{O}^{+++}\cdot\text{SO}_4^{--})/(\text{RSO}_4^+)$, but this is impossible to decide from the data. Assuming that the ratio is unaltered by NaClO_4 and is given by the value of Q_e at 0.05 *M* SO_4^{--} , the quotient K_{11} for expt. 1, Table III is calculated as 16, and for expt. 2 of the same table, at somewhat lower ionic strength as 20. The large change in K_{11} from the conditions of expt. 11 to those obtaining in the experiments of Table III, is in line with the large value of $\Delta s^\ddagger$ for reaction (II).

The data of Table IV suggest that salts do affect the ratio $(\text{RH}_2\text{O}^{+++}\cdot\text{SO}_4^{--})/(\text{RSO}_4^+)$. While in dilute solution (expts. 1, 2, 3, Table IV) NaClO_4 and NaHSO_4 influence Q_e in approximately the same way, in more concentrated solution (expts. 4, 5, 6) replacing NaClO_4 by NaHSO_4 enhances the ratio. For concentrated electrolyte solutions effects due to changes in the activity of water must become important. The decrease in Q_e as the concentration of sulfuric acid is increased is attributable, in part at least, to this cause.

Over the composition range investigated, which includes variation of the initial concentration of Co(III) from 0.0150 to 0.00150 as well as the variation in concentrations of other ions, the reactions are first order in (Co(III)) . Using solutions at lower (SO_4^{--}) than we have in our rate study, Adell⁷ observed k_A to be independent of SO_4^{--} , and k_S to be given by an expression of the form $k^0 f(\text{SO}_4^{--}) (\text{RH}_2\text{O}^{+++})$, where f is a function taking account of interionic attraction effects. For the conditions we have adopted, $\text{RH}_2\text{O}^{+++}$ is almost completely associated with SO_4^{--} , so that the net change (except for further association of

Co(III) and SO_4^{--}) is represented in equation (I). The data of Table I exhibit the interesting feature that k_A and k_S are about equally affected by the concentration of sulfate ion for solutions in which Co(III) can be presumed to be almost completely associated with SO_4^{--} . The catalytic effect of sulfate ion is best demonstrated by observing its effect on k_A for solutions at constant ionic strength. Comparison of expts. 1, 2 and 3 of Table III shows that SO_4^{--} increases the rate of removal of SO_4^{--} from the inner coordination sphere. Catalysis by anions of substitution reactions in complex ions has been observed in other cases.^{7,8}

The two series of experiments in Table IV show the influence of H^+ in increasing the lability of the system. The effect is attributable specifically to H^+ rather than HSO_4^- , since it decreases as (SO_4^{--}) increases. The specific effect of H^+ is not great (and is not expected to be great since the H^+ has only a slight affinity for SO_4^{--}), and did not appear over the variation in (H^+) executed by Adell⁸ in dilute electrolyte solution. The differences in lability observed for solutions containing K^+ , Na^+ and Mg^{++} are probably significant, and indicate increasing interaction between cation and SO_4^{--} in the order presented. The results in very acidic solution show general trends which are consistent with the ideas presented. It may be noted in addition, that the relatively slight increase in k_A from 6.0 *M* H_2SO_4 to 9.0 *M* H_2SO_4 is attributable to the decrease in activity of the water.

Comparison of the specific rates at the two temperatures leads to values of E and Q at 0.05 *M* SO_4^{--} corresponding to k_A and k_S of 19.3 ± 0.5 and 23.7 ± 0.5 kcal./mole, and 10^{10} and $10^{13.6}$ l. mole⁻¹ min.⁻¹. The change from $\text{RH}_2\text{O}^{+++}\cdot\text{SO}_4^{--}$ to RSO_4^+ has a normal frequency factor and the over-all entropy change must appear in the entropy of activation for the reverse change. This implies that the charge separation in the activated state is closer to that in $\text{RH}_2\text{O}^{+++}\cdot\text{SO}_4^{--}$ than it is in RSO_4^+ . This in turn is more in line with an activated state of coordination number 5 rather than with one of 7.⁴

An original purpose in undertaking the kinetic investigation of the present system was to attempt to distinguish $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms on the basis that at high SO_4^{--} , a limiting rate would be expected (governed by the rate of formation of a presumed intermediate, such as $\text{Co}(\text{NH}_3)_5^{+++}$ for the $\text{S}_{\text{N}}1$ mechanism, whereas on the $\text{S}_{\text{N}}2$ mechanism, such a limiting rate would not be expected. The effort to make such a distinction on kinetic evidence is vitiated however by the association of $\text{RH}_2\text{O}^{+++}$ and SO_4^{--} which, in effect, changes the nature of the reactants. However, in view of the demonstrated effect of SO_4^{--} in increasing lability of the system, the observation that the rate of water exchange is diminished when it occurs in the presence of the net change to RSO_4^+ becomes stronger evidence for an important contribution by the $\text{S}_{\text{N}}1$ mechanism.⁴

Various comparisons which can be made makes it seem likely that the observations recorded here on

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(8) R. A. Plane and H. Taube, *J. Phys. Chem.*, **66**, 53 (1962).

the equilibrium between inner sphere and outer sphere complex ions will find their counterpart in labile systems of the same charge type, as for example $\text{Fe}^{+++}\text{-SO}_4^-$ and $\text{Ce}^{+++}\text{-SO}_4^-$. In general the equilibrium behavior of $\text{Co}(\text{NH}_3)_6\text{H}_2\text{O}^{+++}$ in association reactions with anions is very nearly the same as for other tripositive ions forming 1:1 complexes. Thus, the equilibrium constant for association with Cl^- at 25° and $\mu = 0.05$ is 4.1^9 and the association reaction is slightly endothermic. This behavior is in striking similarity to that of $\text{Fe}^{+++}\text{-Cl}^-$.¹⁰ Furthermore, for $\text{Co}(\text{NH}_3)_6^{+++}$ the affinities decrease in order from Cl^- to I^- , as they do for Fe^{+++} . The association constant observed¹¹ for La^{+++} and SO_4^- at $\mu = 1.00$ and 25° is 25 and for Ce^{+++} and SO_4^- under the same conditions is

17.5.¹² In the present system in the same salt environment (but at 31.1°) the constant for association involving outer sphere complexes is only 16, and if the inner sphere complexes are included, the constant would be roughly doubled. These similarities strengthen the view that for the labile systems consisting of SO_4^- and tripositive ion, the ratio of concentrations of inner and outer sphere forms will also be of the order of magnitude of unity.

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